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The spectra and structure of sulphur-containing organic compounds—I. The vibrational spectra of dimethylsulphite and dimethylsulphite-d_6

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Abstract—The i.r. spectra of $(CH_3O)_2SO$ in crystalline state and of $(CD_3O)_2SO$ in liquid and crystalline states as well as the Raman spectra of $(CH_3O)_2SO$ and of $(CD_3O)_2SO$ in liquid state have been investigated. Two crystalline modifications of $(CH_3O)_2SO$ and of $(CD_3O)_2SO$ have been obtained. The i.r. spectra of oriented crystalline films have been investigated in polarized light. The vibrational spectra of $(CH_3O)_2SO$ and $(CD_3O)_2SO$ have been interpreted and their force fields obtained on the basis of more complete experimental data.

INTRODUCTION

The i.r. spectra of dimethylsulphite (DMS) in gaseous and liquid states as well as in solvents of different polarity have been studied in [1–8], the Raman spectrum of liquid DMS is given in [1] (depolarization degree of Raman lines has not been determined). The presence of dynamic equilibrium of two rotational isomers has been established. However, the vibrational spectrum of DMS in crystalline state has not been described and no data on the vibrational spectra of dimethylsulphite-d_6 (DMS-d_6) have been presented.

The present paper is devoted to the investigation of the i.r. spectra of crystalline DMS, of the i.r. spectra of liquid and crystalline DMS-d_6 and of the Raman spectra of liquid DMS and DMS-d_6. The spectra have been interpreted on the basis of the more complete experimental data and the force field of these molecules has been determined, its tentative evaluation having been made in [6].

EXPERIMENTAL

The i.r. spectra and the Raman spectra have been obtained in exactly the same way as in Reference [9]. In order to record absorption spectra in polarized i.r. light crystal samples have been grown by a slow cooling down of the liquid film. Crystalline films formed by a single crystallization center have been investigated. When several crystal nuclei appeared the sample temperature was increased to the melting point after which the sample was cooled down again. The degree of film monocrystallinity has been determined by visual control in crossed polaroids [10].

RESULTS AND DISCUSSION

Figures 1 and 2 and Tables 1 and 2 present the i.r. and Raman spectra of DMS and DMS-d_6 in liquid state. The Raman spectrum of DMS is simular to the one obtained before [1], with the exception of the weak bands at 398, 515, 770, 1195 and 2835 cm^{-1} observed by us.

The i.r. spectra of DMS and DMS-d_6 in crystalline state have not been observed before, since no crystalline state could be obtained by cooling down the thin film of liquid: the sample vitrified when the temperature was lowered to 80°K [3, 7]. However by means of repeated cooling of the liquid film (sample training) with a simultaneous visual observation in the crossed polaroids we succeeded in selecting the temperature at which DMS and DMS-d_6 are crystallized.

Two crystalline modifications of DMS and DMS-d_6 have been obtained: crystal I and crystal II. Their i.r. absorption spectra in polarized light are presented in Figs 3 and 4 and Tables 1 and 2. The spectra of crystals I and II differ in the shift of the 460, 1430, 2837, 2995, 3011, 3040 cm^{-1} bands for DMS and the 410 and 438 cm^{-1} bands for DMS-d_6, as well as in the appearance of multiplet structures of the 585, 1147, 1204 cm^{-1} bands. The spectra also differ in the 1400 and 3000 cm^{-1} (DMS) and the 440, 890, 1100, 2200, 2300 cm^{-1} regions (DMS-d_6).

Repeated growing of crystal films shows that the probability of the formation of crystal I and II is roughly equal. Both modifications are stable over the temperature range from 80 K to melting point (~180 K). No phase transition of one modification to the other has been observed. In the case of repeated growing of monocrystal films of crystal I or II i.r. spectra have been obtained whose absorption bands differ in intensity. This is due to different orientation of the crystal film relative to the KBr plates [11].

The additional splitting of i.r. absorption bands in the crystal II spectra as compared with the crystal I spectra (see the 1450 and 3000 cm^{-1} regions (Fig. 3, Table 1) and the 1060 and